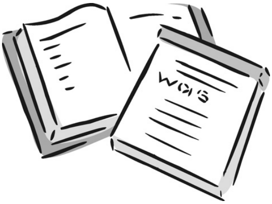
KÉMIA IDEGEN NYELVEN



Kémia németül

Szerkesztő: Horváth Judit

Az előző szám fordítását még **2023. január 9**-ig be lehet küldeni.

Kémia angolul

Szerkesztő: Tóth Edina

A fordításokat **2023. január 9**-ig lehet a kokel.mke.org.hu honlapon keresztül feltölteni.

A ritkaságok, amikről órán nem beszélünk

Majd minden évben akadnak lelkes kilencedikesek, akik a kémiatanárnak szegezik a kérdést: „És róluk mikor fogunk tanulni?” A róluk mindig az atipikus, a ritka, a szokatlan, amiről sajnos nem tanulunk. Az f-mező az egyik ilyen „ritkaság”. Ha rákérdeznek a miért nemre, általában annyit tudunk mondani, mert igen komplikált elemi állapotban előállítani őket. Az új fordítási téma tehát a lantanoidák.

A kitűzött szöveg egy több, mint 20 éves és meglehetősen hosszú tudományos cikk kivonata. A tudományos cikkekben nagyszámú utalás található más kutatók munkájára. Ezt évszámmal és a szerző nevével teszik meg. Amennyiben a hivatkozott információ nem egyetlen személy munkája *„XY et al”*, vagyis *„XY és társai”* megjelölést használnak. A cikk által használt jelölésrendszerben szerepel az anyagmennyiség-koncentráció elavult jelölése: *M* a mol/dm^3 helyett.

4. Applications of Separation Techniques for Lanthanides: Basic Chemistry and Methods

Analysis to determine the rare-earth content of materials can have many different objectives. Successful separations require a judicious combination of appropriate group separation/preconcentration, separation of individual members of the series, and the proper detection technique. Recent reviews that are readily available in the chemical literature offer compilations of "cookbook" methods for conducting analyses of samples of different types. In the following sections, we will offer a brief summary of preferred methods for specific types of analyses and provide appropriate literature references for the reader to pursue for details beyond those offered herein. [...]

4.1 Geological samples

There are three general motivations for analysis of natural samples: (1) exploration for rare-earth mineral resources, (2) isotopic analysis for elucidation of the geological history of the earth, and (3) analysis of living samples to investigate natural distribution of lanthanides in the biosphere. The analysis of geologic samples for rare-earth content has obvious implications for rare-earth mining, and rare-earth analyses also have been applied to petroleum geology (Emery and Robinson 1993), but one vital area of rare-earth analyses is the scientific inquiry into geological problems.

The chemical and nuclear properties of rare-earth elements make them excellent tracers of geologic processes. Little differentiation in rare-earth concentrations is observed in commonly encountered low-temperature processes like mineral weathering. The chemical similarity of the trivalent rare-earth cations that makes analytical separations difficult, ensures that rare earths generally follow each other in geochemical cycles, though large anomalies in Ce or Eu concentrations are commonly observed because of the formation of Ce^{4+} and Eu^{2+} under oxidizing or reducing conditions, respectively. At higher temperatures, however, the rare-earth element compounds can be fractionated based on melting points, under geothermal conditions, or on volatility, under extra-terrestrial conditions. Each of these mechanisms gives different systematic enrichments or depletions of certain rare earths. By studying the fractionation patterns of the rare-earth elements, the origin of the processes that formed a mineral phase can be ascertained with important implications for solar evolution. An application of this methodology can be found in Haskin's (1989) review of the rare-earth abundances in lunar surface samples.

While the naturally occurring rare earths are widely considered non-radioactive, seven of them, La, Ce, Nd, Sm, Gd, Dy, and Lu, have naturally occurring radioactive isotopes. Of these, ^{138}La ($t_{1/2}$ = $1.06 \cdot 10^{11}$ yr), ^{147}Sm ($t_{1/2}$ = $1.08 \cdot 10^{11}$ yr), and ^{176}Lu ($t_{1/2}$ = $3.7 \cdot 10^{10}$ yr) have half-lives short enough to be useful isotopic tracers for both geo- and cosmochemistry The stable progeny of these radioactive parents are analyzed by mass spectrometry, and they must be free of other isobaric interferences (^{142}Ce, ^{144}Sm, ^{148}Sm, and ^{150}Sm interfere with determination of ^{142}Nd, ^{144}Nd, ^{148}Nd, and ^{145}Nd) as a 0.03% deviation in the ^{143}Nd/^{144}Nd isotopic ratio corresponds to 100 million years in the Sm/Nd isochron (Emery and Robinson 1993). The ^{147}Sm/^{143}Nd pair is the most widely employed and is of great importance in lunar and meteoric chronology and evolution (Patchett 1989). Because Sm and Nd are both light rare-earth elements with only one important oxidation state, they follow each other closely in geochemical cycles.

[...]

Analysis in support of mineral exploration typically involves standard techniques for both rock dissolution and chromatographic analysis. For example, Moraes and Shihomatsu (1994) report the analysis of US Geological Survey standard rock samples using ion-pair chromatography (dynamic ion exchange) with hiba [abbreviation for alpha-hydroxyisobutyric acid] as the eluant. Standard procedures for rock dissolution, preconcentration, and chromatographic analysis are followed. A gradient elution (pH=3.8, [hiba]= 0.07-0.4 M at 1ml/min over 20 minutes) was employed with colorimetric detection for post-column derivatization. Each lanthanide was resolved, though there was slight overlap between Y and Dy The detection limits in the original samples were in the 1-3 ppb range. This technique is a representative recent demonstration of the general technique developed by Cassidy and co-workers in the 1980s (Cassidy et al 1985, Cassidy 1988, Barkley et al 1986, Cassidy and Chauvel 1989, Knight et al 1984). It relies on the basic chemistry introduced in the 1950 S (Choppin and Silva 1956). The same basic method (using slightly different gradient conditions) was used by Al-Shawi and Dahl (1994), Kuroda et al (1990) and Moraes et al

(1997) for analysis of monazite/phosphate rock, the latter using solvent extraction for preconcentration of the lanthanides. Kuroda et al (1990) employed an oxalate precipitation step to isolate the lanthanides from the sulfuric acid dissolver solution. Oguma et al (1993) analyzed silicate rocks using a glycolic acid concentration gradient at pH=3-5, though Sm, Eu, Gd, Tb, and Dy are not resolved, and Ho poorly so le Roex and Watkins (1990) employed a mixed oxalate/diglycolate eluant but experienced incomplete resolution of Ho from Y and Lu from Yb. By adding dipicolinic acid to the eluant, they were able to complete the analysis in a somewhat extended period without complete removal of transition metal impurities.

[...]

Isotopic analysis of rock samples provides unique insights into the genesis and evolution of the earth. This method is perhaps the most demanding of all lanthanide analyses, as it typically requires chemical separation of the group from the matrix, individual members of the series, and usually relies on mass spectrometric detection.

The separation chemistry is generally comparable to that applied for less demanding samples/objectives. The detection method requires careful preparation of the post-separation sample to avoid potential interferences. In fact, the MS detection technique is extremely sensitive to the presence of impurities, requiring that essentially all impurities be removed.

4.2 Analysis for materials science

By comparison with natural samples, lanthanide-bearing species from manufactured sources are typically much simpler analytical targets. The samples are often more readily dissolved and, because many of them are rare-earth-based materials, preconcentration steps can sometimes be eliminated. Recent reports have applied analytical separation methods to determine lanthanide concentrations in metals (Kobayashi et al 1992), alloys (Al-Shawi and Dahl 1996), and magnets (Saraswati 1993), in high-purity rare-earth oxides (Stijfhoorn et al 1993, Yin et al 1998, W Li et al 1997, 1998, Wu et al 1997, Peng et al 1997), and in optical materials (Bruzzoniti et al 1996).

Light lanthanide metals are alloyed with magnesium to increase structural strength and reduce corrosion (Al-Shawi and Dahl 1996). The alloy sample dissolved readily in 20 % HNO_3. The resulting clear solution was diluted and subjected to ion chromatographic analysis using isocratic hiba solutions as the eluant. Analysis was complete in less than 15 minutes and gave good separation of all alloy components including lanthanides, Zn, Cu, Mn, and Mg. Such alloys are commonly analyzed for their rare-earth content using X-ray fluorescence or optical techniques [...]

Chromatographic analysis offers substantial cost saving (for instrumentation) and simple operation making this option attractive. The Nd-Fe-B magnets are among the highest-strength permanent magnets available today. The coercivity (a measure of magnet strength) of the magnets is altered by trace amounts of Tb, Dy, Ho, Er, or Yb making analysis of these species either in the magnet or in magnet precursors highly desirable. Saraswati (1993) has reported an ion-chromatographic procedure for analysis of both transition metals and rare-earth metal ions in a single chromatogram. [...] The transition metals and lanthanide ions are surprisingly well-separated in the reported chromatograms, particularly in light of the relatively weak sensitivity that lanthanide tartrate stability constants indicate for the changing ionic radius of the cations. [...] The system is also somewhat noteworthy in the remarkably good separation between the transition metals and the rare earths.

4.3 Nuclear applications

Among the most common by-products of nuclear fission are several of the lanthanide metal ions, particularly the light members of the series. Fission yields of selected metal ions among these are very well known. Analysis of dissolved irradiated fuel elements for their lanthanide content can be applied to monitor the status of a nuclear reactor. The application of chromatographic techniques to intensely radioactive samples offers several unique challenges. With the application of radiometric detection techniques, the sensitivity of chromatographic methods can be appreciably extended, at least for short half-life nuclides. The basic analytical procedures for chromatographic analysis of irradiated fuels were developed during the 1980s at the Chalk River laboratory in Canada.

[...]

In addition to their use as fission yield monitors, radioactive rare-earth isotopes can be used to monitor the concentrations of other fission products. Strontium-90 ($t_{1/2}$ = 29 yr) is one of the most prevalent fission products and is a particular concern for bioaccumulation because of the high-energy radiation it emits and because it mimics the chemistry of Ca, an essential element. As it decays, ^{90}Sr comes to radioactive equilibrium with its also radioactive progeny, 90Y ($t_{1/2}$=64 h), so that the radioactivity attributable to ^{90}Sr and ^{90}Y is equal after 30 days. The radioactivity of ^{90}Y interferes with radiometric measurements of the ^{90}Sr concentration, and thus they must be separated before analysis. To avoid the problem of new ^{90}Y growing into a purified ^{90}Sr sample, which would always complicate direct radiometric ^{90}Sr determination, the ^{90}Sr concentration is determined from the radioactivity of ^{90}Y after separation from ^{90}Sr.

[...]

Source of Text:

Handbook on the Physics and Chemistry of Rare Earths, volume 28 Elsevier, 2000 Edited by: Karl A. Gschneidner, Jr. and LeRoy Eyring (ISBN: 978-0-444-50346-6)

180. Kenneth L. Nash and Mark P. Jensen: Analytical separations of the lanthanides: basic chemistry and methods